



QUANTUM MECHANICS AND SPECTROSCOPY: VIBRATION-ROTATION SPECTRUM

AIMS

- (a) To determine spectroscopic parameters of CO, by analyzing a large amount of data, and compare these with literature values.
- (b) Determine molecular structure from spectroscopic parameters.

SKILLS USED IN THIS EXERCISE

- Peak-picking and interpretation of FTIR spectra and data analysis using Python.
- Writing an introduction and abstract.

INTRODUCTION

For a *diatomic molecule* A–B, the harmonic vibrational frequency is given by

$$\omega_e = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \quad (1)$$

where: c is the velocity of light (in units of cm s^{-1});

k is the force constant (N m^{-1}) of the A–B bond;

the reduced mass μ (kg) is expressed in terms of the masses m_A and m_B of atom A and atom B,

$$\mu = \frac{m_A m_B}{m_A + m_B} \quad (2)$$

The general anharmonic oscillator is described by energy levels (with respect to the minimum of the potential) obeying an expansion in $(v + 0.5)$, where $v \geq 0$ is the vibrational quantum number

$$G(v) = \omega_e(v + 0.5) - \omega_e x_e(v + 0.5)^2 + \omega_e y_e(v + 0.5)^3 \dots \quad (3)$$

The fundamental vibrational frequency ω (in cm^{-1}) is given by:

$$G(1) - G(0) = \omega_e - 2\omega_e x_e + \dots \quad (4)$$

Where the anharmonicity is small ($\omega_e x_e$ typically $\lesssim 10 \text{ cm}^{-1}$), the fundamental vibrational frequency ω is close to ω_e .

Diatomic molecules may also rotate, and exhibit a set of rotational energy levels that depend on the angular momentum quantum number $J \geq 0$. In the rigid rotor limit:

$$B_v = B_v J(J + 1) \quad (5)$$

where B_v is the rotational constant in vibrational state, v . The rotational constant, B_v is related to the bond length, r_v ,

$$B_v = \frac{1}{hc} \frac{\hbar^2}{2\mu r_v^2} = \frac{h}{8\pi^2 \mu r_v^2} \quad (6)$$

where μ is the reduced mass and the factor of $1/hc$ converts energy to cm^{-1} . Thus, c must be used in units of cm s^{-1} . The fact that we label the rotational constant with the vibrational state label implies that the rotational constant, and hence effective bond length, changes for different vibrational states. You will explore this in the experiment. This relation (6) can also be used to convert B_e to r_e , where the subscript “e” refers to the quantity at the equilibrium position (i.e. the bottom of the anharmonic well). The rotational constant, B_v , depends slightly on the vibrational quantum number,

$$B_v = B_e - \alpha_e(v + 0.5) \quad (7)$$

where α_e is called the vibration-rotation interaction constant.

Vibration-Rotation Energies

The rotation-vibration energy levels are given by

$$S(v, J) = G(v) + F(J) = \left(v + \frac{1}{2}\right)\omega + B_v J(J + 1) \quad (8)$$

in the harmonic oscillator, rigid rotor limit.

Now, when a molecule such as CO absorbs an infrared photon, angular momentum must be conserved. As such, the angular momentum of the molecule must change. This gives rise to two types of transition: those that *increase* the angular momentum, and those that *decrease* the angular momentum.

The set of transitions that *increase* the angular momentum are called the *R*-branch, and these transitions generally lie to *higher* energy than the vibrational band origin. The set of transitions that *decrease* the angular momentum are called the *P*-branch, and these transitions generally lie to *lower* energy than the vibrational band origin.

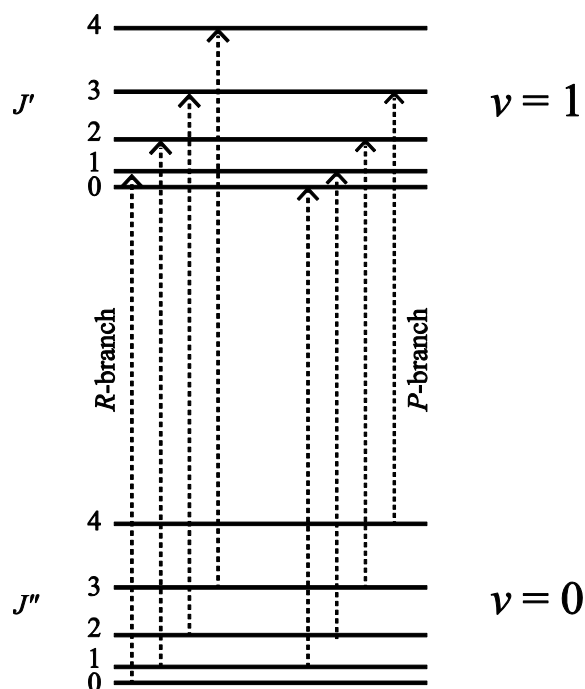


Figure 1 – The vibration-rotation transitions of a diatomic molecule.

Denoting the upper state angular momentum quantum number J' and the lower state angular momentum quantum number J'' , a general formula may be written for the vibration-rotation transition.

$$\begin{aligned}\Delta S &= S(v', J') - S(v'', J'') \\ &= G(v') + B_v J'(J' + 1) - G(v'') - B_v J''(J'' + 1)\end{aligned}\quad (9)$$

For the fundamental vibration transition,

$$\Delta S = \omega + B_1 J'(J' + 1) - B_0 J''(J'' + 1) \quad (10)$$

Now, the energies of the *R*-branch and *P*-branch may be written

$$\begin{aligned}\Delta S_R &= \omega + (B_1 - B_0)J''^2 + (3B_1 - B_0)J'' + 2B_1 \\ \Delta S_P &= \omega + (B_1 - B_0)J''^2 - (B_1 + B_0)J''\end{aligned}\quad (11)$$

Conveniently, if we introduce a dummy quantum number, $x = -J''$ for the P-branch and $x = J'' + 1$ for the R-branch, we obtain

$$\Delta S = \omega + (B_1 - B_0)x^2 + (B_1 + B_0)x \quad (12)$$

for both branches, which allows us to analyze them simultaneously.

You will measure the wavenumber of these transitions, assign them, and then analyze the data to determine the parameters ω , B_1 , B_0 and thus r_e , the equilibrium bond length!

RESULTS

Import the spectral data into the Jupyter notebook, both available through Moodle. Follow the notebook instructions.

Concentrate on the structure in the 2150 cm^{-1} region of the spectrum (zoom in using `xmin` and `xmax`). The resolution should be sufficient to discern the individual rotational lines.

Use the peak-picking code to determine the positions of all significant features in the spectrum. Assign the lower and upper-state quantum numbers, J'' and J' . Do this for both the *R*- and *P*-branches. To aid your analysis, the first line in the *R*-branch should be $J'' = 0$ located near 2147 cm^{-1} . Remember to adjust the `offset` for the *P*-branch so that the first line is $J'' = 1$.

Store the picked wavenumbers (cm^{-1}) in the array `energy`. Create a new quantum number x , which will allow both sets of data to be plotted together on the same curve. Plot `energy` vs x . Is it smooth? If not, check the assignments of the lowest J'' lines.

ANALYSIS

Create a global fit modelling Equation 11 using the provided code and plot it with the experimental data. Determine ω , B_1 and B_0 , then B_e and compare it to the literature value ($B_e = 1.93128087\text{ cm}^{-1}$).

You can finesse the model by adding extra terms to the fit which will improve it, but you can decide if they are necessary. This accounts for higher order terms not present in the rigid rotor model, such as centrifugal distortion, D . At high rotational quantum numbers the bond gets stretched and the effective rotational constant goes down. D is therefore related to the stiffness of the bond, $D = 4B^3/\omega_e^2$.

1. From the information in the Introduction section of these notes, determine r_1 and r_0 , the average bond lengths in these vibrational states. Estimate their error (they will be the same percentage error as the rotational constants).
2. Determine r_e and α_e .

DISCUSSION

3. Calculate the expected frequency of a pure rotational $J = 1 \rightarrow 0$ emission. Research how this frequency is used in astronomy – why is it important?
4. Model the temperature using the provided code to adjust the Boltzmann term $k_B T$ (in cm^{-1}) such that the maximum intensity occurs at the same J'' as your experimental data. Convert $k_B T$ to Kelvin. Is it reasonable?

REPORT

Answer the online Quiz associated with this exercise.